

Discussion of Applicability of Elements Tested to Encompass Entire Periodic Table: Particular Applicability to All Metals Including Light Metals

“According to modern quantum theory, the chemical and physical properties of substances arise fundamentally from electrodynamic interactions. Modifying these interactions can alter electronic structures and thereby endow the elements of the periodic table and their compounds with new properties”

Professor Dudley R. Herschbach
Frank B. Baird Professor of Science, Harvard University
Chemistry Nobel Laureate, 1986

Introduction: Periodic Law:

“If all the elements are assembled in order of atomic number, it can be noticed that there is a relationship in properties corresponding to the atomic number.”¹

Key to Metals Task Force & INI International

In 1829 J. W. Döbereiner stated that there existed some three-element groups, or triads, in which the atomic weight of the middle element was the average of the other two and the properties of this element lay between those of the other two. The English chemist J. A. Newlands found (1863-65) that if the elements are listed according to atomic weight starting with the second, the 8th element following any given element has similar chemical properties, and so does the 16th. This became known as the law of octaves. About the same time, A. E. de Chancourtois arranged the elements according to increasing atomic weight in the form of a vertical helix with eight elements in a turn, so that elements having similar properties fell along vertical lines.

D. I. Mendeleev was the first to state the periodic law close to its present form. He proposed in 1869 that the properties of elements are periodic functions of the atomic weight and grouped the elements in a periodic system. The work (1913-14) of H. G. Moseley on the X-ray spectra of elements led to the present form of the periodic law based on atomic numbers. “Today, the periodic law is explained on the basis of the electronic structure of the atom, which is believed to be the main factor underlying the chemical properties and many of the physical properties of the elements. In turn, the electronic structures of atoms have been successfully accounted for by quantum theory”².

¹ <http://www.key-to-metals.com/Article122.htm>, ©1999-2005 INI International

² <http://www.encyclopedia.com/doc/1E1-periodlw.html>, taken from The Columbia Encyclopedia, Sixth Edition Date: 2008.

Figure 1 below demonstrates the relationship between the frequency of x-rays emitted by atoms which have been energized in an electrical arc. Each type of atom (each element) emits a few characteristic frequencies of x-rays, which differ from one atom to the next. The lowest x-ray frequency emitted by each element is found to increase with increasing position in the periodic table.³

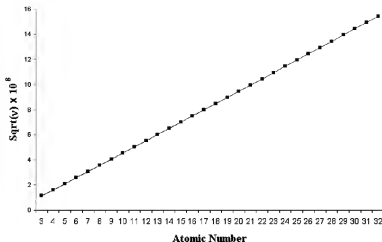


Figure 1: The relationship between X-ray emission frequency and atomic number

While, Figure 1 demonstrates the importance of increasing atomic number, in particular to spectral analysis, Figure 2 demonstrates the importance of orbital filling to the physical properties of an element. The periodic nature of elemental behavior is demonstrated as the ionization energy of elements is shown as a function of atomic number. Clearly, the valence electrons (i.e., the outermost electrons) are instilling the physical properties of the elements based on the occupied orbitals.

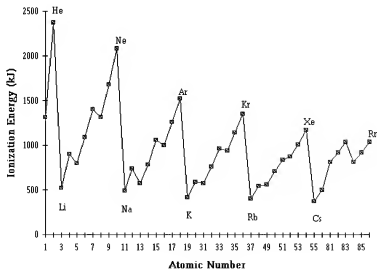


Figure 2: Ionization energy as a function of atomic number clearly demonstrates periodic nature of elements and dependence of physical properties on atomic orbital filling and valence (outermost) electrons.

³ The Structure of the Atom, by John S. Hutchinson, September, 2006. <http://cnx.org/content/m12433/latest/>.

Classical and Modern Orbital Theory:

*"...the properties of elements are determined by the occupied levels of highest energy: the electrons filling the s and p levels in each row (and sometimes those filling d levels) are traditionally called valence electrons and determine chemical properties."*⁴

Electronic Structure and Properties of Solids

Orbitals refer to the spatial wave function of an electron in an atom (or molecule). Within quantum mechanical theory, waves can only exist if the properties of the systems allow such energetic states. While the current patent application is applicable to elements in their most fundamental state in some systems, the interatomic spacing and the atomic charge of the material allows only electrons of certain wavelengths to exist (i.e., the basis for LCAO, linear combination of atomic orbitals). For the atom, in a quantum-mechanical context, the electron energy eigenstates are described as angular momentum eigenstates, making it possible to classify all energy eigenstates by means of two quantum numbers, ℓ^5 and m . For any value of ℓ and m , there are many different energy eigenstates, described by the integer n , in order of increasing energy, where n is called the principal quantum number. Figure 3 below demonstrates the unique energy levels characteristic of orbital filling (wave functions).

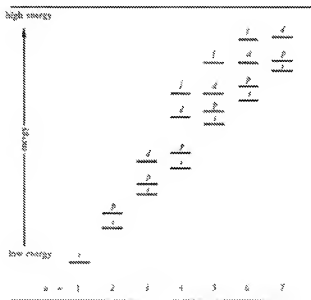


Figure 3: Relative energies of orbitals in neutral atoms. The branched lines show the number of orbitals (energy levels) represented by each line.

⁴ *Electronic Structure and the Properties of Solids, The Physics of the Chemical Bond*, Walter A. Harrison, p. 15 (1989) ISBN 0-486-66021-4.

⁵ In common terminology, $\ell=0$ corresponds to the s state; $\ell=1$, the p state; $\ell=2$, the d state; and $\ell=3$, the f state. These letters were derived from the spectroscopic characteristics of the lines: sharp, principal, and diffuse.

*"The filling of successive levels is the essence of periodic variation in the properties of elements as the atomic number increases."*⁶

Electronic Structure and Properties of Solids

To better understand the electronic states systematically in elements other than hydrogen, envision the charge of the hydrogen nucleus being increased element by element, with a corresponding addition of an electron every time the nuclear charge is increased by one unit e . The filling of successive atomic orbitals is described by the "Aufbau" principle. As an atom is progressively built up by adding electrons, as needed, they occupy orbitals that produce the most stable configuration of the atom. According to this principle, electrons fill orbitals starting at the lowest available orbital before occupying higher energy orbitals to produce the lowest energy state (i.e., the $1s$ is filled before the $2s$ orbital). Orbitals are filled according to the Madelung rule ($n+l$ rule) where orbitals with a lower $n+l$ value are filled prior to those with higher $n+l$ values; a value determined by the total number of nodes in the $n+l$ atomic orbital which is a function of its relative energy.

The Pauli exclusion principle limits the number of electrons that can occupy a single orbital. In the event of degenerate orbitals of the same energy, Hund's rule dictates that unoccupied orbitals will be filled before occupied orbitals by electrons having different spins. For example, copper and chromium represent known exceptions to the Aufbau principle. Elemental copper should have 9 electrons in its $3d$ orbital but its electronic configuration is $[\text{Ar}].3d^{10}.4s^1$ instead of $[\text{Ar}].3d^9.4s^2$ because of the greater stability of a half-filled rather than a fully-occupied orbital. Similarly, chromium assumes the electron configuration $[\text{Ar}].3d^5.4s^1$ instead of $[\text{Ar}].3d^4.4s^2$. Significantly, both of these elements obey the Madelung ($n+l$) rule ($n+l=5$) because the last determining electron occupies a $3d$ orbital. These exceptions would be more apparent if the electronic configurations were determined in the strict order of orbital filling ($[\text{Ar}].4s^1.3d^{10}$ for copper and $[\text{Ar}].4s^1.3d^5$ for chromium). The Madelung rule also holds true for a number of other elements that represent exceptions: $n+l=6$ for Nb, Mo, Ru, Rh, Pd, Ag; $n+l=7$ for La, Ce, Gd, Au, and $n+l=8$ for Ac, Th, Pa, U, Np and Cm.

Figure 4 again demonstrates the periodic nature of chemical properties correlating directly with the filling of atomic orbitals.

⁶ *Electronic Structure and the Properties of Solids, The Physics of the Chemical Bond*, Walter A. Harrison, p. 15 (1989) ISBN 0-486-66021-4

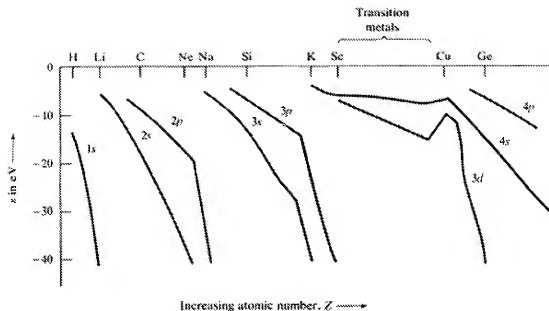


Figure 4: Trends in the variation of atomic term values in (atomic orbital energies) in electron volts (data from Herman and Skillman, 1963).

In computational physics and chemistry, the Hartree-Fock (HF) method is an approximate method for the determination of the ground-state wave function and ground-state energy of a quantum many-body system. The Hartree-Fock method is applied to the solution of the electronic Schrödinger equation of atoms, molecules, and solids. Typically, in modern Hartree-Fock calculations, the one-electron wave functions are approximated by a linear combination of atomic orbitals (called Slater-type orbitals). More recently, Gaussian-type orbitals, that are less computationally intensive, were introduced in the mid seventies by Pople (Nobel Laureate).

The origin of the Hartree-Fock method dates back to the end of the 1920s, soon after the derivation of the Schrödinger equation in 1926. In 1927 D.R. Hartree introduced a procedure, which he called the self consistent field method, to calculate approximate wave functions and energies for atoms and ions. Hartree was guided by some earlier, semi-empirical methods of the early 1920s (by E. Fues, R.B. Lindsay and himself) set in the old quantum theory of Bohr. In the Bohr model of the atom, the energy of a state with principal quantum number, n is given in atomic units as $E = -1/n^2$. It was observed from atomic spectra that the energy levels of many-electron atoms were well-described by applying a modified version of Bohr's formula. By introducing the quantum defect, d as an empirical parameter⁷, the energy levels of a generic atom were well approximated by the formula $E = -1/(n+d)^2$, in the sense that one could reproduce fairly well the observed transitions levels observed in the X-ray region. Subsequent researchers introduced other potentials containing additional empirical parameters with the hope of better reproducing the experimental data. Hartree sought to do away with empirical parameters and solve the many-body time-independent Schrödinger equation from fundamental physical principles, i.e. *ab initio*.

⁷The existence of a non-zero quantum defect was attributed to electron-electron repulsion which clearly does not exist in the isolated hydrogen atom. This repulsion resulted in partial screening of the bare nuclear charge.

The properties of solids (e.g., conductivity, color, critical temperature, etc.) are often described using band theory. While the electrons of a single free-standing atom occupy atomic orbitals to form a discrete set of energy levels, when several atoms are brought together into a molecule, their atomic orbitals split, as in a coupled oscillation, producing molecular orbitals proportional to the number of atoms. The number of orbitals becomes exceedingly large, and the difference in energy between them becomes very small, so the levels may be considered to form continuous *bands* of energy rather than the discrete energy levels of the atoms in isolation. However, some intervals of energy contain no orbitals, no matter how many atoms are aggregated, forming *band gaps*. The location of the Fermi level⁸ with respect to these energy bands and energy gaps, is what imposes many of the physical properties of a solid (See Figure 5). The density of states of a system describes the number of states at each energy level that are available to be occupied. A high DOS at a specific energy level means that there are many states available for occupation. Today, many theorists use density functional theory (DFT) that typically represents an improvement over HF theory, with energy refinements that utilize more highly electron-correlated *ab initio* methods such as couple cluster calculations (CCSD)⁹. These advanced computational methods can today successfully calculate, from first principles, many of the basic properties of materials. Throughout history and independent of models used, the periodic variation of physical properties with increasing atomic number (Z) persists derived from the fundamental orbital structure.

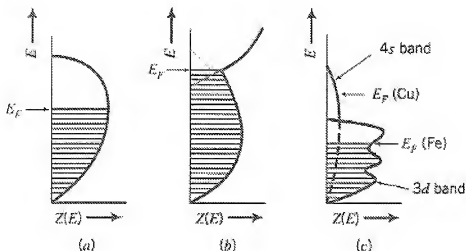


Figure 5: Schematic density of states curves $Z(E)$ and the Fermi Energy (E_F) for (a) monovalent metal (b) divalent metal (c) 3d transition metals such as Cu¹⁰

⁸ The Fermi level in quantum mechanics is typically described as the maximum electron energy at absolute zero $T=0$. For conductors, the Fermi level falls in an energy band; for insulators, the Fermi level falls within an energy gap.

⁹ <http://www.chemieurope.com/lexikon/c/Hartree-Fock>, 2006-2008 Chemie DE Information Service GmbH, a Life Science Network Division.

¹⁰ *The Electronic Properties of Engineering Materials*, James D. Livingston, Chapter 14, p 256, John Wiley & Sons, 1999.

Experimental Program: Applicability to All Metals Including Light Metals

Figure 6 below shows the elements that have been successfully tailored to modify the physical and/or chemical property set according to the methods specified in US patent #6,921,497. A set of pure elements and alloys were methodically subjected to the aforementioned methods to ensure that from a quantum mechanics viewpoint, nearly the entire spectrum of the periodic table was covered¹¹. Note that the alkali metals, the alkaline earth metals, the transition metals, and light metals were tested. In fact, the individual elements actually tested represent >75% of the commercially-relevant, readily-available commodity “metals” used today.

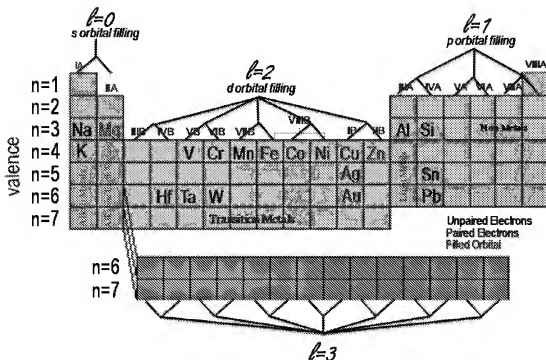


Figure 6: Periodic table showing all elements tailored. Notes elements tested spanned multiple groups and traversed periods.

Several series of elements were tested to validate the broad applicability of tailoring. In the transition metals¹², almost an entire period was tailored, from Vanadium through Zinc. This series includes unpaired outer electrons (V, Cr, Mn) and paired outer electrons (Fe through Zn). Zn represents a filled d-block while Cr and Cu represent exceptions to orbital filling (e.g., $4s^1d^5$ and $4s^1d^{10}$ versus $4s^2d^4$ and $4s^2d^9$; see discussion above regarding known exceptions to the Aufbau principle). A series of heavier

¹¹The successive electron occupation of the f-orbital (lanthanide and actinide series) was not tested.

¹²In metals, when outer shells are filled before the inner shells are completely occupied, the element is known as a transition metal.

transition elements, Hf, Ta, W, were tested to confirm tailoring in the presence of a completely filled f-orbital. Also within the transition elements, a group (IB) was sequentially tested (Cu, Ag, Au), to confirm tailoring in the presence of successive d-orbital occupation. Alkali and alkaline earth elements were tailored beginning with sodium and going across the period (i.e., filling the s-orbital) to magnesium and going down the period to potassium (i.e., demonstrating effects on heavier elements and sequential orbital filling). To complete the spectrum of elements tested, the light metals (e.g., Al, Sn, Pb) and a non-metal (Si) were tested to validate the effect of tailoring as the p-orbitals are filled¹³. Si demonstrated tailoring in the absence of an occupied d-orbital; Sn represented tailoring in the presence of an occupied d-orbital, but the absence of an occupied f-orbital; Pb demonstrated tailoring in the presence of a full-complement of occupied orbitals: s, p, d, and f; with relativistic effects dominating property character. By following an experimental protocol spanning multiple periods and groups and a wide variety of atomic orbitals, the entire spectrum of the periodic table has been essentially covered.

The property changes induced by tailoring in representative elements strongly suggest that all metals (including light metals) can be tailored successfully. This supposition is consistent with known chemical principles dating from the 1800's (Periodic Law) and current understanding of quantum theory of electronic structures (Hartree-Fock, see Table 1).

¹³ Graphitic carbon, C₆₀, has also been tailored subsequent to the submission of this original patent application.

Hartree-Fock term values after Mann (1967), in eV. In the upper part, ϵ_s values are given first for each element and ϵ_p values are given next; for the transition metals, ϵ_d values are given first and ϵ_s values are given second.

						He	Li			
						24.97	5.34			
						-----	-----			
	Be	B	C	N	O	F	Ne	Na		
	8.41	13.46	19.37	26.22	34.02	42.78	52.51	4.95		
	---	8.43	11.07	13.84	16.72	19.86	23.13	---		
	Mg	Al	Si	P	S	Cl	Ar	K	Ca	Sc
	6.88	10.70	14.79	19.22	24.01	29.19	34.75	4.01	5.32	5.72
	---	5.71	7.58	9.54	11.60	13.78	16.08	---	---	---
Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr	Y
6.49	7.96	11.55	15.15	18.91	22.86	27.00	31.37	3.75	4.85	5.34
---	---	5.67	7.33	8.98	10.68	12.43	14.26	---	---	---
Ag	Cd	In	Sn	Sb	Te	I	Xe	Cs	Ba	La
5.98	7.21	10.14	13.04	16.02	19.12	22.34	25.69	3.36	4.29	4.35
---	---	5.37	6.76	8.14	9.54	10.97	12.44	---	---	---
Au	Hg	Tl	Pb	Bi	Po	At	Rn			
6.01	7.10	9.82	12.48	15.19	17.96	20.82	23.78			
---	---	5.23	6.53	7.79	9.05	10.33	11.64			

TRANSITION METALS										
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	
	9.35	11.04	12.55	13.94	15.27	16.54	17.77	18.96	13.36	
	5.72	6.04	6.32	6.59	6.84	7.08	7.31	7.52	6.49	
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	
	6.80	8.46	10.03	11.56	13.08	14.59	16.16	17.66	14.62	
	5.34	5.68	5.95	6.19	6.39	6.58	6.75	6.91	5.98	
	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	
	6.62	8.14	9.57	10.96	12.35	13.73	15.13	16.55	14.17	
	5.41	5.72	5.98	6.19	6.38	6.52	6.71	6.85	6.01	

Table 1: The atomic orbital energies, in eV, calculated at the HF level with refined boundary conditions leading to slightly more accurate values than those provided graphically in Figure 4 (data from Herman and Skillman, 1963) for transition metals.